

APPLICANTS

AVECIA LIMITED

TITLE

Phthalocyanines And Their Use In Ink-Jet Printers

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This invention relates to inks, to dyes, to printing processes, to printed substrates and to ink-jet printer cartridges.

5 Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

Colour ink-jet printers typically use four inks of differing hues: magenta, yellow, cyan, and black. Colours other than these may be obtained using differing combinations of these inks. Thus, for optimum print quality, the colourants used must be able to form  
10 an ink with a specific precise hue. This can be achieved by mixing colourants but is advantageously achieved by used a single colourant with the exact hue required.

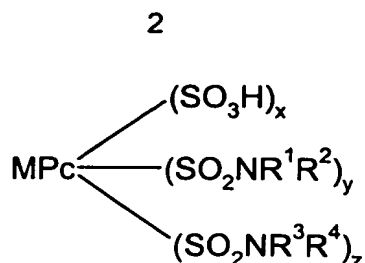
With the advent of high-resolution digital cameras and ink-jet printers it is becoming increasingly common to print off photographs using an ink-jet printer. This avoids the expense of conventional silver halide photography and provides a print quickly  
15 and conveniently.

While ink-jet printers have many advantages over other forms of printing and image development there are still technical challenges to be addressed. For example, there are the contradictory requirements of providing ink colorants that are soluble in the ink medium and yet do not run or smudge excessively when printed on paper. The inks  
20 need to dry quickly to avoid sheets sticking together after they have been printed, but they should not form a crust over the tiny nozzle used in the printer. Storage stability is also important to avoid particle formation that could block the tiny nozzles used in the printer. Furthermore, the resultant images desirably do not fade rapidly or change their shade on exposure to light or common oxidising gases such as ozone.

25 WO99/67334 describes a new class of phthalocyanine that displays considerable promise in ink-jet printing. One phthalocyanine in particular, which carries sulfo, sulfonamide and hydroxyethyl sulfonamide substituents, seems to have an optimum balance of the properties required in a dye for use in ink-jet printing.

We have surprisingly found that when dyes of this type bear these substituents  
30 only in the  $\beta$  position of the phthalocyanine ring they have superior ink-jet printing characteristics when compared to the randomly substituted dyes as described in WO99/67334 and the  $\beta$ -substituted dyes bearing only sulfo and sulfonamide substituents as described in WO02/060994.

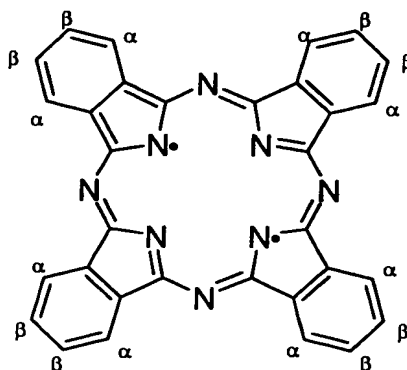
Thus, the present invention provides a composition comprising:  
35 (a) a major dye component which is a mixture of phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

- 5            M        is Cu or Ni;  
              Pc       represents a phthalocyanine nucleus of formula



- 10            R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;  
              R<sup>4</sup> is optionally substituted C<sub>1-4</sub>-hydroxyalkyl;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

- 15            the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached to a β position on the phthalocyanine ring; and

(b) a liquid medium which comprises water, water and an organic solvent or an organic solvent free from water.

- 20            Phthalocyanine dyes bearing sulpho, sulfonamide and substituted sulfonamide substituents are usually prepared by sulfonating a phthalocyanine pigment followed by chlorination and then amination/amidation. The product of this reaction is a complex mixture that carries sulpho, sulfonamide and substituted sulfonamide substituents in any susceptible position on the phthalocyanine ring (for example see Schofield, J and Asaf, M in Journal of Chromatography, 1997, 770, pp345-348).

- 25            Details of the usual route for forming a dye of Formula (1) may be found in WO99/67334, Example 1, which is incorporated herein by reference.

The phthalocyanine dyes of Formula (1) where the substituents are attached to a β position on the phthalocyanine ring may be prepared by any method known in the art, and

particularly by cyclisation of appropriate  $\beta$  substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable source of ammonia (if required), a copper or nickel salt, for example  $\text{CuCl}_2$ , and a base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) followed by chlorination and then amination/amidation.

Preferably phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a  $\beta$  position on the phthalocyanine ring are prepared by cyclisation of 4-sulfo-phthalic acid to phthalocyanine  $\beta$ -tetrasulfonic acid. The phthalocyanine  $\beta$ -tetrasulfonic acid is then chlorinated and the sulfonyl chloride groups so formed are reacted with compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are as hereinbefore defined. This reaction is preferably performed in water at a pH above 7. Typically the reaction is performed at a temperature of 30 to 70°C and is usually complete in less than 24 hours. The compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  may be used as a mixture or added sequentially.

Many of the compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  are commercially available, for example ammonia and ethanolamine, others may be made easily by a skilled person using methods which are well known in the art.

The ratio of sulfo to the two-sulfonamide substituents may be varied independently by varying the nature and amount of chlorinating agent used, the relative amounts of compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  used and the reaction conditions in both reactions.

A skilled person will appreciate that the product of these reactions will be a disperse mixture and so the values of x, y and z will represent an average of the groups present in the mixture.

When phthalocyanine  $\beta$ -tetrasulfonic acid is an intermediate in a route to dyes of Formula (1) it may be chlorinated by reacting with any suitable chlorinating agent.

Chlorination is preferably carried out by treating the phthalocyanine  $\beta$  tetrasulfonic acid with chlorosulfonic acid preferably in the presence of an acid halide such as thionyl chloride, sulfuryl chloride, phosphorous pentachloride, phosphorous oxychloride or phosphorous trichloride.

Preferably M is Cu.

Preferably  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or methyl, more preferably  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are all H.

$\text{R}^4$  may comprise more than 1 hydroxy group, although preferably  $\text{R}^4$  comprises a single hydroxy.

Preferably  $\text{R}^4$  is unsubstituted  $\text{C}_{1-4}$ -hydroxyalkyl, more preferably  $\text{C}_2$ -hydroxyalkyl.

Preferred optional substituents which may be present on  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently selected from: optionally substituted alkoxy (preferably  $\text{C}_{1-4}$ -alkoxy), optionally substituted aryl (preferably phenyl), optionally substituted aryloxy (preferably phenoxy), optionally substituted heterocyclic, polyalkylene oxide (preferably polyethylene

oxide or polypropylene oxide), carboxy, phosphato, sulfo, nitro, cyano, halo, ureido, -SO<sub>2</sub>F, hydroxy, ester, -NR<sup>5</sup>R<sup>6</sup>, -COR<sup>5</sup>, -CONR<sup>5</sup>R<sup>6</sup>, -NHCOR<sup>5</sup>, carboxyester, sulfone, and -SO<sub>2</sub>NR<sup>5</sup>R<sup>6</sup>, wherein R<sup>5</sup> and R<sup>6</sup> are each independently H or optionally substituted alkyl (especially C<sub>1-4</sub>-alkyl). Optional substituents for any of the substituents described for R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be selected from the same list of substituents.

When R<sup>3</sup> is optionally substituted C<sub>1-4</sub>alkyl then preferably R<sup>3</sup> is unsubstituted C<sub>1-4</sub>-hydroxyalkyl, more preferably R<sup>3</sup> is C<sub>2</sub>-hydroxyalkyl.

It is especially preferred that R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are all H and R<sup>4</sup> is C<sub>1-4</sub>-hydroxyalkyl, particularly -CH<sub>2</sub>CH<sub>2</sub>OH.

Preferably x has a value of from 0.2 to 3.8. More preferably x is less than 1.8 and especially less than 1.2. It is particularly preferred that x is less than 1.

Preferably y has a value of from 0.2 to 3.8 and more preferably of from 0.5 to 3.5.

Preferably z has a value of from 0.2 to 3.8 and more preferably of from 0.5 to 3.5.

In the dyes of Formula (1) the  $\alpha$ -positions of the phthalocyanine ring are preferably unsubstituted, that is they carry a hydrogen substituent.

The dyes of Formula (1) are also preferably free from fibre reactive groups. The term fibre reactive group is well known in the art and is described for example in EP 0356014 A1. Fibre reactive groups are capable, under suitable conditions, of reacting with the hydroxyl groups present in cellulosic fibres or with the amino groups present in natural fibres to form a covalent linkage between the fibre and the dye. As examples of fibre reactive groups excluded from the dyes of Formula (1) there may be mentioned aliphatic sulfonyl groups which contain a sulfate ester group in beta-position to the sulfur atom, e.g. beta-sulfato-ethylsulfonyl groups, alpha, beta-unsaturated acyl radicals of aliphatic carboxylic acids, for example acrylic acid, alpha-chloro-acrylic acid, alpha-bromoacrylic acid, propiolic acid, maleic acid and mono- and dichloro maleic; also the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, beta-chloro and beta-bromopropionic acids and alpha, beta-dichloro- and dibromopropionic acids or radicals of vinylsulfonyl- or beta-chloroethylsulfonyl- or beta-sulfatoethyl-sulfonyl-endo- methylene cyclohexane carboxylic acids. Other examples of cellulose reactive groups are tetrafluorocyclobutyl carbonyl, trifluoro-cyclobutenyl carbonyl, tetrafluorocyclobutylethenyl carbonyl, trifluoro-cyclobutenylethenyl carbonyl; activated halogenated 1,3-dicyanobenzene radicals; and heterocyclic radicals which contain 1, 2 or 3 nitrogen atoms in the heterocyclic ring and at least one cellulose reactive substituent on a carbon atom of the ring, for example a triazinyl halide.

Acid or basic groups on the dyes of Formula (1), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the dyes in free acid and in salt form.

Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as

$((\text{CH}_3)_4\text{N}^*)$  and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The dyes may be converted into a salt using known techniques.

5 The dyes of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.

When the preferred route, as set out above, is used to synthesise dyes of Formula (1) then they are predominantly formed as ammonium salts. However, any known techniques may be used to exchange ammonia for another cation for example, acidification, optionally followed by dialysis, to remove the original cations with  
10 subsequent addition of alternative cations (e.g. by addition of alkali metal hydroxide, ammonium salt or amine). Use of ion exchange resins and reverse osmosis are other techniques for cation exchange.

Preferably the liquid medium (b) comprises water and an organic solvent or an organic solvent free from water.

15 When the liquid medium (b) comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-  
20 miscible organic solvents include  $\text{C}_{1-6}$ -alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene  
25 glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono- $\text{C}_{1-4}$ -alkyl ethers of diols, preferably mono- $\text{C}_{1-4}$ -alkyl ethers of diols  
30 having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and  
35 sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono-  $\text{C}_{1-4}$ -alkyl and  
40  $\text{C}_{1-4}$ -alkyl ethers of diols, more preferably mono-  $\text{C}_{1-4}$ -alkyl ethers of diols having 2 to 12

carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP-A-425,150.

5           When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50° to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic  
10           solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH<sub>2</sub>Cl<sub>2</sub>; and ethers, preferably diethyl ether; and mixtures thereof.

          When the liquid medium comprises a water-immiscible organic solvent then preferably a polar solvent is preferably included since this enhances solubility of the dye of  
15           Formula (1) in the liquid medium. Examples of polar solvents include C<sub>1-4</sub>-alcohols.

          It is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C<sub>1-4</sub>-alkanol, more especially ethanol or propanol).

          The organic solvent free from water may be a single organic solvent or a mixture  
20           of two or more organic solvents. It is preferred that when the liquid medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a liquid medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

          Liquid media comprising an organic solvent free from water are particularly useful  
25           where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

          The liquid medium may of course contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or  
30           non-ionic.

          Although not usually necessary, further colorants may be added to the ink to modify the shade and performance properties. Examples of such colorants include C.I. Direct Yellow 86, 132, 142 and 173; C.I. Direct Blue 307; C.I. Food Black 2; C.I. Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko  
35           Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International.

          If the composition of the present invention contains phthalocyanine dyes other than those of Formula (1) then preferably at least 70% by weight, more preferably at least 80% by weight, especially at least 90% by weight, more especially at least 95% by weight and particularly at least 99% by weight of the total amount of phthalocyanine dye is of  
40           Formula (1) wherein the substituents, represented by x, y and z are attached to a β

position on the phthalocyanine ring.

It is preferred that the composition according to the invention is an ink suitable for use in an ink-jet printer. Ink suitable for use in an ink-jet printer is an ink which is able to repeatedly fire through an ink-jet printing head without causing blockage of the fine nozzles.

An ink suitable for use in an ink-jet printer preferably has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C.

An ink suitable for use in an ink-jet printer preferably contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a colorant of Formula (1) or any other component of the ink).

Preferably an ink suitable for use in an ink-jet printer has been filtered through a filter having a mean pore size below 10 $\mu$ m, more preferably below 3 $\mu$ m, especially below 2 $\mu$ m, more especially below 1 $\mu$ m. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

Preferably an ink suitable for use in an ink-jet printer contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions.

Preferred compositions comprise:

(a) from 0.01 to 30 parts of dyes of Formula (1); and

(b) from 70 to 99.99 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

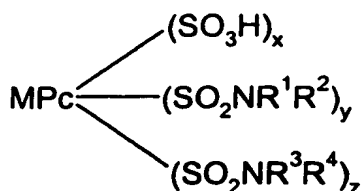
Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

The inks may be incorporated in an ink-jet printer as a high concentration cyan ink, a low concentration cyan ink or both a high concentration and a low concentration ink. In the latter case this can lead to improvements in the resolution and quality of printed images. Thus the present invention also provides a composition where component (a) is present in an amount of 2.5 to 7 parts, more preferably 2.5 to 5 parts (a high concentration ink) or component (a) is present in an amount of 0.5 to 2.4 parts, more preferably 0.5 to 1.5 parts (a low concentration ink).

Compositions according to the present invention yield prints that display a good fastness to water and light. In particular, prints prepared using these inks display excellent light and ozone fastness.



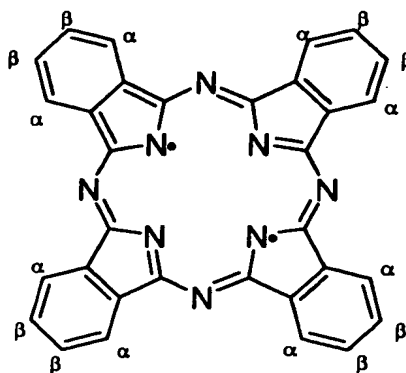
A second aspect of the invention provides a mixture of dyes of Formula (2) and salts thereof:



Formula (2)

wherein:

M is Cu or Ni;  
Pc represents a phthalocyanine nucleus of formula



$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or optionally substituted  $\text{C}_{1-4}$ alkyl;

$\text{R}^4$  is optionally substituted  $\text{C}_{1-4}$ -hydroxyalkyl;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached to a  $\beta$  position on the phthalocyanine ring.

M,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ , x, y and z are all as preferred in the first aspect of the invention, it is particularly preferred that x is less than 1.

In the dyes of Formula (4) the  $\alpha$ -positions on the phthalocyanine ring are unsubstituted, that is they bear a H.

It is especially preferred that  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are all H and  $\text{R}^4$  is  $-\text{CH}_2\text{CH}_2\text{OH}$ .

The dyes of Formula (2) have attractive, strong cyan shades and are valuable colorants for use in the preparation of ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light. In particular they display excellent light and ozone fastness.

A third aspect of the invention provides a process for forming an image on a

substrate comprising applying an ink suitable for use in an ink jet printer, as described in the first aspect of the invention, thereto by means of an ink-jet printer.

5 The ink-jet printer preferably applies the ink to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal  
10 causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as described in International Patent Application WO00/48938 and International Patent Application WO00/55089.

15 The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Glossy papers are especially preferred.

It is most preferred that the paper is photographic quality paper.

20 A fourth aspect of the present invention provides a material preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers printed with a composition according to the first aspect of the invention, a dye according to the second aspect or by means of a process according to the third aspect of the invention.

25 It is especially preferred that the printed material of the fourth aspect of the invention is a photograph printed by a process according to the third aspect of the invention.

30 A fifth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is an ink suitable for use in an ink-jet printer, as defined in the first aspect of the present invention. The cartridge may contain a high concentration ink and a low concentration ink, as described in the first aspect of the invention, in different chambers.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

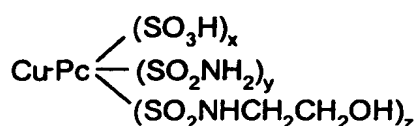
#### Example 1

##### 35 Analysis of dyes of Formula (1)

Confirmation of the structure of dyes of Formula (1) is by mass spec. Elemental analysis is used to determine the ratios of x to y + z. Thus, when the sum of x plus y and z is not exactly 4 this is thought to be due to the presence of impurities. The presence of these impurities and their effect on the estimated values of x, y and z would be well known  
40 to a person skilled in the art who would appreciate that the value of x plus y plus z should

not exceed 4 and who would treat the experimentally determined values of x, y and z as indicative of the true ratios of the groups. Also with some dyes according to the present invention it is not possible, using these methods, to discriminate between the different sulfonamide substituents. In these cases x and y are either quoted as a sum of both sulfonamide groups i.e. (y + z) or are quoted as half the total sulfonamide detected i.e. y = 1.4av, in this latter case y and z will always be given as the same value.

Preparation of the following dye substituted only in the  $\beta$  position wherein x is 1.0, and (y + z) is 3.4:



Stage 1 - Preparation of copper phthalocyanine substituted with 4-SO<sub>3</sub>H groups in the  $\beta$  position

Potassium 4-sulfo-phthalic acid (56.8g), urea (120g), CuCl<sub>2</sub> (6.9g), ammonium molybdate (1.2g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (7.5g) were mixed in a reaction vessel. The mixture was then warmed in stages (130°C/30 minutes, 150°C/30 minutes, 180°C/30 minutes, 220°C) over 2 hours and the melt which formed was stirred at 220°C for a further 2 hours. The solid which formed was extracted 4 times with hot water (4 x 200ml) and the extract was filtered to remove insoluble material. The resultant filtrate was stirred at between 60°C – 70°C and then sufficient NaCl was added to give a 7% salt solution. Stirring was continued and the solid that precipitated was filtered, washed with a 10% salt solution (200 ml) and pulled dry by vacuum. The resultant damp solid (77.6g) was slurried in acetone, filtered and dried first at room temperature and then at 50°C.

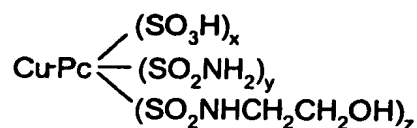
Stage 2 Preparation of the title product

Phosphorous oxychloride (2.43g) was added dropwise to chlorosulfonic acid (54.3g) over 5-10 minutes while keeping the temperature below 30°C. When all the POCl<sub>3</sub> had been added, the product of stage 1 (21g) was added portion-wise while keeping the reaction temperature below 60°C, this addition took 20-30 minutes. The reaction mixture was stirred at 50-60°C for 15-20 minutes. The temperature of the reaction mixture was then gradually increased to 138-140°C over 30 minutes and the reaction mixture was stirred at this temperature for 3 hrs 30 minutes. The mixture was then allowed to cool to room temperature and stirred overnight. A further portion of POCl<sub>3</sub> (1.2 ml) was added to the reaction mixture which was reheated to 138°-140°C and stirred for a further 1 hour 30 minutes. The mixture was then cooled to room temperature and added to a mixture of

water/ice/NaCl/ concentrated HCl (100ml/200g/5g/3ml). The solid that precipitated was filtered, washed with ice cold acidified 5% salt solution and pulled dry using a vacuum pump. The resultant damp paste was added portion-wise to a mixture of ethanolamine/35% ammonia solution /water (1.25g/1.3ml/200ml) at 0°-10°C. The mixture was adjusted to pH 8.5 and stirred at 10° to 20°C for 18 hours. The reaction mixture was then warmed to 40 ± 2°C and the pH was adjusted to 12.8-13.0 with 2M NaOH and stirred for 5-6 hours. At the end of this time sufficient NaCl was added to the reaction mixture to give a 20% solution and the pH was adjusted to less than 1 with concentrated HCl. The solid which precipitated was filtered, washed with an acidified 10% salt solution (pH < 1) and pulled dry using a vacuum pump. The resultant damp solid was dissolved in deionised water at pH 7, dialysed, filtered and then dried at 50°C to give 12.6g of product.

### Example 2

Preparation of the following dye substituted only in the β position wherein x is 0.7 and (y + z) is 3.4:



20

The procedure of Example 1 was repeated except that in stage 2 the following amounts of reagents were used:

Copper phthalocyanine substituted with 4-SO<sub>3</sub>H groups in the β position  
from stage 1 – 11.8g

25 Chlorosulfonic acid - 69.9g

POCl<sub>3</sub> - 6.99g

Ethanolamine - 1.61g

Concentrated ammonia solution (35%) – 0.8g

### 30 Examples 3 to 10

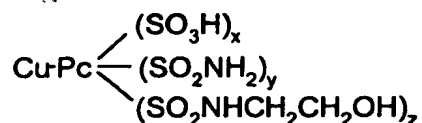
Examples 3 to 10 were prepared using an analogous process to that described in Example 1 except that in stage 2 an alternative amine was used in place of ethanolamine and the molar equivalent of the amino compound and ammonia were adjusted as shown in Table 1. Table 1 also shows the ratio of the substituents represented by x, y and z.

35 In the case of Examples 3 and 4 it was not possible to discriminate between y and z and so an average value is given for each parameter.

	Amine	Mol. Eq. Amine	Mol. Eq. Ammonia			
				x	y	z
Example 3	NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	3.3	0.5	1.5	1.4av	1.4av
Example 4	NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	2.2	1.1	1	1.8av	1.8av
Example 5	H <sub>2</sub> NCH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	3.3	0.5	0.7	0.6	2.9
Example 6	H <sub>2</sub> NCH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	2.5	1.1	0.4	0.5	3.5
Example 7	H <sub>2</sub> NC(CH <sub>2</sub> OH) <sub>3</sub>	3.3	0.5	1.9	0.9	1.6
Example 8	H <sub>2</sub> NC(CH <sub>2</sub> OH) <sub>3</sub>	2.5	1.1	ND	ND	ND
Example 9	HN(CH <sub>3</sub> )CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	2.2	1.1	0.8	1.1	2.5
Example 10	HN(CH <sub>3</sub> )CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	3.1	0.5	0.6	0.5	3.1

### Comparative Example

5 The comparative Example was prepared, as in Example 1 of International Patent Application WO99/67334, by sulfonation of copper phthalocyanine pigment followed by amination/amidation a process which results in a dye of formula:



10 wherein the substituents are in both the  $\alpha$  and  $\beta$  positions and where x is 2.7, y is 0.5 and z is 0.8.

### Inks

#### Example 11

#### Preparation of Ink 1 and the Comparative Ink

15 The dye of Example 2 and the dye of the Comparative Example were converted into inks by dissolving 3g of dye in 100 ml of a liquid medium comprising:

Thiodiglycol	5 %
2-Pyrrolidone	5 %
20 Surfynol™ 465	1 %
Water	89 % (all % by weight)

and adjusting the pH of the ink to pH 8 with sodium hydroxide. An ink of this composition would be expected to have a viscosity of between 1 to 3 cp. Surfynol™ 465 is a surfactant from Air Products Ltd.

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### Ink-Jet Printing

Ink 1 and the Comparative Ink were filtered through a 0.45 micron nylon filters and then incorporated into empty print cartridges using a syringe.

The inks were then ink-jet printed onto Epson Premium Glossy Photopaper ("SEC PM") and Canon PR101 Photopaper ("PR101").

The prints, at 100%, were tested for ozone fastness by exposure to 1ppm ozone at 40 °C, 50% relative humidity for 24hrs in a Hampden 903 Ozone cabinet. Fastness of the printed ink to ozone was judged by the difference in the optical density before and after exposure to ozone.

Light-fastness of the printed image was assessed by fading the printed image in an Atlas Ci5000 Weatherometer for 100 hours and then measuring the change in the optical density.

Optical density measurements were performed using a Gretag spectrolino spectrophotometer set to the following parameters :

Measuring Geometry :	0°/45°
Spectral Range :	400 - 700nm
Spectral Interval :	20nm
Illuminant :	D65
Observer :	2° (CIE 1931)
Density :	Ansi A
External Filler :	None

Light and Ozone fastness are assessed by the percentage change in the optical density of the print, where a lower figure indicates higher fastness, and the degree of fade. The degree of fade is expressed as  $\Delta E$  where a lower figure indicates higher light fastness.  $\Delta E$  is defined as the overall change in the CIE colour co-ordinates L, a, b of the print and is expressed by the equation  $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{0.5}$ . Results for light and ozone fastness are shown below.

#### Light Fastness

	Delta E PR101	%OD Loss PR101	Delta E SEC PM	%OD Loss SEC PM
Ink 1	5	-3	4	3
Comparative Ink 1	20	29	5	13

#### Ozone Fastness

	Delta E PR101	%OD Loss PR101	Delta E SEC PM	%OD Loss SEC PM
Ink 1	0	0	1	3
Comparative Ink 1	51	58	23	41

Clearly dyes according to the present invention display both enhanced ozone and light fastness compared to dyes substituted in both the  $\alpha$  and  $\beta$  positions.

5     **Further Inks**

The inks described in Tables A and B may be prepared using the dyes made in Example 1 to 3. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

10       The following abbreviations are used in Table A and B:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

15       IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

20       BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO =  $\text{Na}_2\text{HPO}_4$  and

TBT = tertiary butanol

TDG = thiodiglycol

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ABLE A

Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
3	10.0	85	3		3	3				5	1	
1	2.1	91		8								1
2	3.1	86	5					0.2	4			5
4	1.1	81			9		0.5		6		9	
1	2.5	60	4	15	3	3			10	10	5	4
2	5	65		20								
5	2.4	75	5	4		5						
1	4.1	80	3	5	2	10		0.3		6		5
2	3.2	65		5	4	6			5	4	6	
6	5.1	96		5						4		5
1	10.8	90	5						5			
2	10.0	80	2	6	2	5					4	
7	1.8	80		5					1		15	
1	2.6	84			11						5	
2	3.3	80	2			10				2		6
8	12.0	90				7	0.3		3			
1	5.4	69	2	20	2	1					3	3
2	6.0	91			4						5	



TABLE B

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	P12
1	3.0	80	15			0.2					5	
2	9.0	90		5						1.2		5
3	1.5	85	5	5		0.15	5.0	0.2				
1	2.5	90		6	4					0.12		
2	3.1	82	4	8		0.3						6
9	0.9	85		10					5	0.2		
1	8.0	90		5	5			0.3				
2	4.0	70		10	4				1		4	11
10	2.2	75	4	10	3				2		6	
1	10.0	91			6						3	
2	9.0	76			7		3.0			0.95	5	
3	5.0	78	5	9							6	
1	5.4	86		11							7	
2	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
4	2.0	90		10								
1	2	88						10				
2	5	78			5			12			5	
5	8	70	2		8			15			5	
1	10	80						8			12	
2	10	80		10								